Identification and Quantification of the Temporal and Spatial Scales of Variability in Particulate and Dissolved Material Associated with Specific Land-Use Activities in the Penobscot River System

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LONG-TERM GOALS

Coastal waters represent the commingling of offshore marine and terrestrial surface source waters and therefore are naturally complex and variable. Our long term goal is to establish observational and modeling approaches to predict sources and scales of variability in the source waters, particularly those related to land use activities in upstream watersheds, from observations and measurements in the coastal waters.

OBJECTIVES

Hydrologic optics provides an approach to characterizing physical and biogeochemical processes in aquatic systems over a range of time and space scales. The linkage between observations of the inherent optical properties (IOPs; absorption, scattering and fluorescence) and the geophysical properties lie in the establishment of robust optical proxies and the quantification of the temporal and spatial scales over which these proxies remain conservative in their properties. Our objectives are to identify and quantify specific optical and chemical characteristics of the colored particulate and dissolved fractions originating in the Penobscot River system that are associated with defined land use activities (land use proxies), and to determine the scales of variability over which these proxies can be detected both temporally (i.e. seasonal and episodic events) and spatially (from the source into coastal waters).

APPROACH

Our approach combines high resolution temporal and spatial hydrographic and optical observations from moored, surface underway and undulating platforms with chemical characterization of the organic and inorganic, particulate and dissolved carbon and nitrogen pools that originate in the sub-watershed drainage basins of the Penobscot River System and flow through Penobscot Bay estuary into the coastal waters of the Gulf of Maine. Our approach is to (1) identify optical proxies for

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bigeochemical parameters, including quantifying the time and space scales of conservative behavior; (2) apply these proxies to high-resolution time and space optical observations to compute concentration and flux of riverborne material into the estuary and coastal systems; (3) compare models for conserved behavior with observations to identify zones and times of non-conserved behavior; (4) elucidate transformation processes at these locations/times; (5) quantify impacts of land use on the biogeochemical properties of the coastal ocean with the goal to predict responses to climate induced hydrologic forcing.

WORK COMPLETED

We have been conducting approximately monthly sampling of 18 stations within the Penobscot River Watershed. At each station discrete water samples are collected for chemical and optical analyses: particulate organic carbon and nitrogen (POC and PON), dissolved organic carbon and nitrogen (DOC and DON), dissolved inorganic nutrients (NO_3, PO_4, SiO_2), fluorometric chlorophyll and pheopigments, total suspended solids and volatile solids (TSS and %VS), particle concentration and size distribution (Sequoia LISST, Agrawal and Pottsmith 2000), spectrophotometric particulate and dissolved absorption, and for selected samples, 3-d excitation/emission fluorescence (Coble 1996; Mayer et al. 1999; McKnight et al. 2001; Baker 2001; 2002a; 2002b). Additionally at each station, a WET Labs triplet sensor (chlorophyll and CDOM fluorescence and 650 nm backscattering) is deployed to obtain an in situ observation for comparison with the chemical and optical properties of the discrete water samples.

Our long-term monitoring program consists of 3 stations within the Penobscot River and Upper Bay instrumented with WET Labs triplet sensors recording hourly observations of chlorophyll and CDOM fluorescence and 660 nm backscattering. These sites include one at the mouth of a major tributary (Sunkhaze River) and two in the main branch of the lower Penobscot River (near West Enfield and Eddington, ME). Over the past year, triplet sensors were deployed at the West Enfield and Eddington, ME sites over the fall of 2006, and were recovered before the winter ice season. Triplet sensors were at all 3 sites redeployed in the summer of 2007.

Under funding provided to co-PI Roesler, we have continued to maintain optical sensors on the existing 3m optical packages on the Gulf of Maine Ocean Observing System (GoMOOS). In particular, we continue to maintain and service optical sensors installed on GoMOOS mooring F, in the mouth of Penobscot Bay under separate funding through a NASA project. Over the past year, we have collected hourly time series of chlorophyll and CDOM fluorescence and NTU scattering sensor as well as 7-channel incident irradiance and upwelling irradiance at GoMOOS mooring F. Using optical time series of CDOM fluorescence and salinity at GoMOOS mooring F, time series of CDOM fluorescence optical data collected from moorings within the Penobscot River, and optical proxy relationships to organic carbon derived from water samples, we have derived models to estimate the flux of organic carbon from the Penobscot River through the Bay (Roesler et al 2006).

As a part of a NASA study examining the transport and transformation of carbon within the Penobscot Bay and surrounding coastal regions, we have been maintaining an inline sampling system on a commercial ship based in Penobscot Bay. Data collected include physical (temperature and salinity) and optical (F_{Chl}, F_{cDOM} and beam attenuation at 660 nm) measurements in the surface waters. This system has provided over 28 large scale transects in the lower Penobscot River and Bay and the Gulf of Maine, and continues to this date.

We have also been conducting field surveys of the lower Penobscot River and western Penobscot Bay in order to characterize the spatial distribution of the dissolved and particulate materials as they flow through the Penobscot River and into the Bay (Figure 1). To date we have conducted 4 intensive field surveys of the region. Over the past reporting period, we have conducted one survey, from 19-21 October 2006.

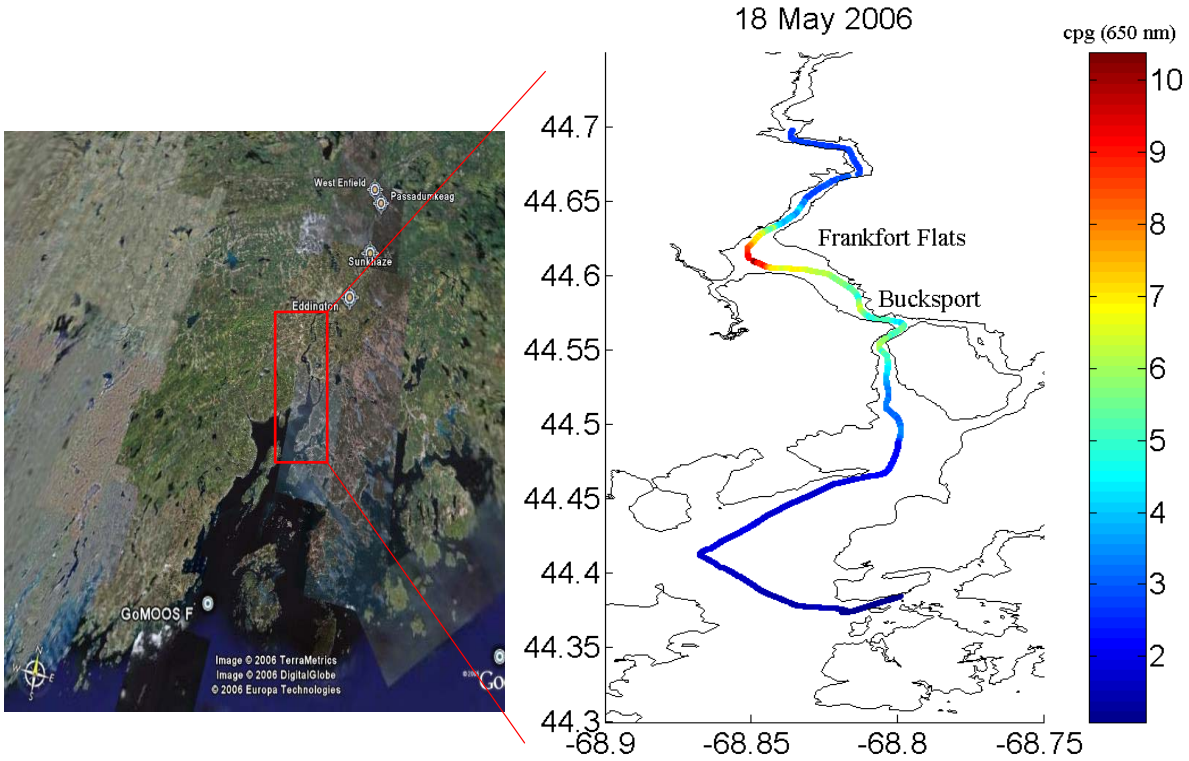

Figure 1. Picture of the Penobscot River and Bay with location of the river moorings (West Enfield, Passadumkeag, Sunkhaze, and Eddington) relative to Penobscot Bay. Inset shows the location of the surface transect data collected on 18 May 2006. Graph shows the surface distributions of beam attenuation (650 nm) in the lower Penobscot River and upper Penobscot Bay collected using the inline system on the RV Argo Maine. Image courtesy of Google Earth.

The field survey was conducted from the RV Argo Maine with our in line sampling system and which was augmented with a hyperspectral absorption/attenuation meter (AC-S) to provide addition spectral resolution in mapping the key optical parameters of the system. We also utilized a WET Labs undulating towed vehicle, called the DOLPHIN, to provide vertical coverage of the upper 1/3 of the water column of temperature, salinity, cDOM, chlorophyll, absorption and beam attenuation and backscattering. Dr. Mark Moline of Cal Poly also participated in this survey, in which he deployed his REMUS AUV to further increase the spatial coverage of the temperature, salinity, chlorophyll and cDOM fluorescence and backscattering of Penobscot Bay. These data provided a detailed view of how the dissolved and particulate material coming out of the Penobscot River mix and interact with the coastal waters. A future field survey is planned for 15-16 November 2007.

RESULTS

Within the watershed, optical proxies have been developed based upon relationships between discrete in situ optical properties measured with a WET Labs triplet sensor (backscattering (bb(660 nm)), fluorescence by colored dissolved organic matter, cDOM (FcDOM) and chlorophyll (FChl), plus associated optical and biogeochemical water sample analyses of the particulate and dissolved matter (i.e. POC, DOC and chlorophyll, respectively). A detailed description of our results are presented in co-PI Roesler's ONR Annual Report for 2007. To summarize, in terms of optical proxies as tracers to watershed type, our results show 1) no spatial or temporal dependence on watershed type to chlorophyll concentration, 2) particle backscattering is a good first order proxy of TSS, 3) there is little dependence on watershed type to total particulate backscattering, 4) F_{cDOM} is good first order proxy for DOC, and shows some dependence on watershed type, and 5) dissolved absorption (412nm) is conserved, and is an excellent tracer of DOC concentration within the river.

Using the combination of carbon-based optical proxies based on the relationships described above and optical data collected from the moored optical sensors in the Penobscot River, Roesler et al (2006) derived models to estimate the flux of organic carbon (partitioned into algal and non-algal particle and dissolved pools). A detailed description of these models and there results are presented in co-PI Roesler's ONR Annual Report for 2007. In summary, in terms of the delivery of optical proxies/carbon from the Penobscot River to the bay, our results show: 1) the river is not a significant source of phytoplankton (or algal carbon) to the bay, 2) the river is a source of POC to the bay, primarily in the non-algal form, and is seasonally variable, and 3) the river is a major source of DOC to the bay which varies seasonally.

Results of our observations to date have suggested that there are significant and traceable differences in the concentration and to a lesser extent the composition of materials entering the Penobscot River via tributary drainage basins and that this material undergoes transformations in the upper portion of Penobscot Bay. A major focus of our efforts has been to characterize the conservative/non-conservative behavior of these materials (dissolved and particulate) through the Penobscot estuary and bay. Our working hypothesis has been that during high flow periods, the material transport rate exceeds the transformation rate and that we can observe clear land use/coverage signals within Penobscot Bay and the coastal waters. However, during low flow periods, transformation exceeds transport and these signals may be degraded within the Bay.

To evaluate this hypothesis, we examined the spatial and temporal trends in our optical proxies using data collected from the inline system installed on the ship of opportunity. Five transects covering the upper portion of Penobscot Bay and the lower Penobscot River were conducted in May, July, August, September and October 2006. Most of these tracks extended north up river past the saltwater tidal range, and thus includes the freshwater endmember. Assuming a two endmember (freshwater and coastal oceanic water) mixing model applies to the Penobscot Bay, then properties which display a linear relationship with salinity across this transect are conserved (transport and mixing), while those that deviate from a simple linear relationship are not conserved (i.e transformed specific properties or exhibiting a source or sink within the system).

Data collected during 2006 are presented in Figure 2. Chlorophyll concentrations entering the bay (freshwater endmember) range from ~ 7 mg/m^3 (May, July, October) to 3 mg/m^3 (September), and steadily declined through the estuary and then increase to levels greater than 7 mg/m^3 in the saltier

waters (Figure 2A). This is most likely due to either blooms occurring within the lower portion of the bay or the influence of coastal phytoplankton blooms being advected into the bay. The optical proxy for particles (beam attenuation, c(660 nm)) shows a more conservative trend with respect to salinity, with the highest values associated with low salinity waters and decrease with increasing salinity (Figure 2B). Note however, that within each sampling period, a large amount of variability typically occurs below salinities of 20 psu, often showing the highest values in the brackish waters.

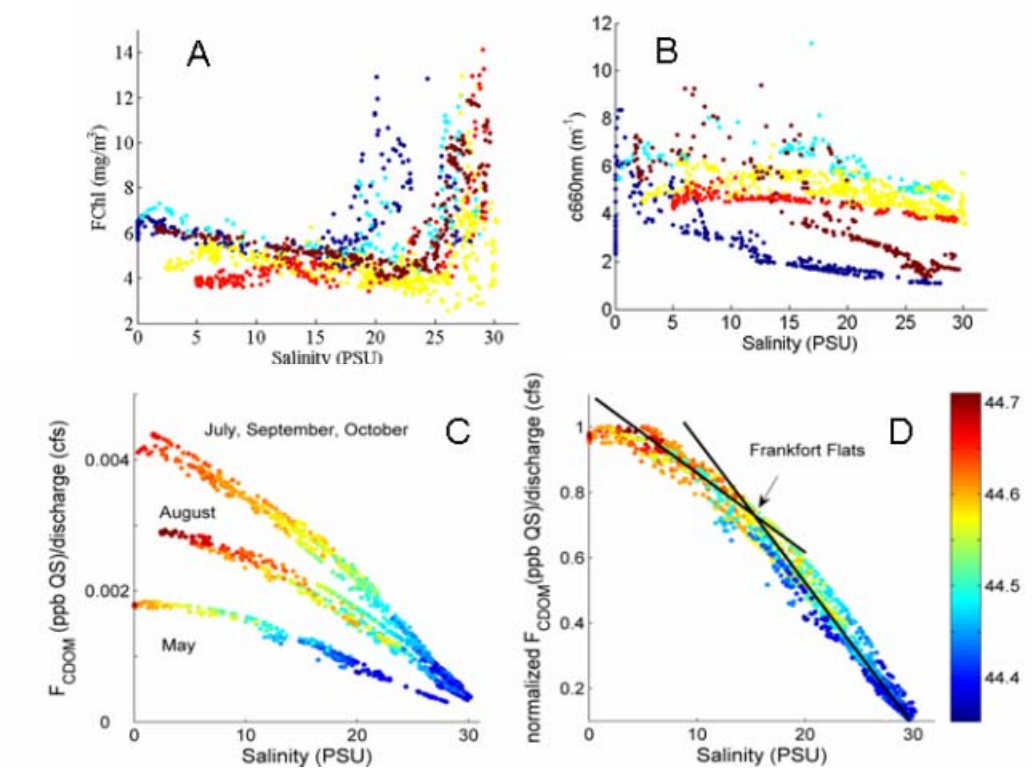

Figure 2. Surface optical properties in the Penobscot estuary during 2006. (A) Chlorophyll distribution versus salinity during May (blue), July (cyan), August (yellow), September (red), and October (dark red). (B) Beam attenuation at 660nm versus salinity (colors same as in A). (C) cDOM fluorescence normalized to Eddington discharge for each of the 5 surface survey periods shown in A. (D) Same as in C, with the cDOM fluorescence normalized to the maximum value during each survey. Piecewise linear fits to observations indicate overlap at geographic location.

The optical property which shows the best correlation with salinity is cDOM fluorescence, regardless of sampling period. The F_{cDOM} proxy for DOC plotted against salinity demonstrates (1) how concentration is discharge dependent and (2) the non-conserved behavior within the estuary. In order to elucidate how much of the seasonal variability in the cDOM fluorescence is due to changes in the volume transport of the Penobscot River, we normalized the cDOM fluorescence data by the discharge (cubic feet per second) measured at the USGS gage station at Eddington, ME for each sampling period (Figure 2C). When normalized to discharge, the seasonal trend in cDOM delivery from the river entering into the bay is maximal in July, September, and October, followed by August, with the lowest values observed in May, again show that the concentration is correlated with discharge. Several studies have shown strongly conservative (linear) relationships between dissolved absorption at 412nm

and/or cDOM fluorescence and salinity for different freshwater inputs, indicating that this proxy can be used as a simple water mass tracer (Coble et al 1998; Twardowski and Donaghay 2001; Blough and Del Vecchio, 2002; Coble et al 2004). However, it is noteworthy that all sampling periods show pronounced non-conservative behavior, indicating that either transformations of the fluorescent DOC are occurring (i.e. that non-fluorescing matter from the river is being transformed to fluorescing matter) or that there is a source of new fluorescent cDOM within the estuary.

There appears to be a distinct change in slope at approximately 15 psu, indicating a source of fluorescent dissolved matter. However, when normalizing the cDOM delivery observations (F_{cdom} / discharge; values plotting in Figure 2C) by the cDOM delivery in at the low river station (F_{cdom} / discharge near the Eddington), the data collapses onto a single curve and the location of slope change is not a specific salinity value (which would imply a chemical process) but a specific geographic location (i.e. Frankfort Flats) suggesting that the transformation processes are likely physically mediated (Figure 2D). Analysis of particle properties, from discrete and in situ observations, in this region show enhanced particle concentrations at all times of the year. It is uncertain if these particles are the result of tidal mixing and resuspension, chemical precipitation or aggregation. However, it is clear that this is a hot spot with respect to DOC transformation and that those transformations are likely to involve significant interaction with particulate matter.

Based on the results above, significant transformations in the optical proxies, and thus the dissolved and particulate pools, appear to be occurring between our lowest sampling station (freshwater endmember) through the estuary to the salt water (oceanic) endmember. During both the May and October intensive field surveys, a non-conservative behavior with salinity was exhibited for the cDOM fluorescence and dissolved absorption at 412nm optical proxies (Figure 3A and B), the latter of which likely indicates non-conserved behavior in DOC, as the dissolved absorption at 412nm was shown to be an excellent proxy for DOC in both the river and bay. As was found for all cruises, on these two specific surveys, the fluorescent dissolved matter appears to have a source in the region of Frankfort Flats, or there is an in situ transformation of nonfluorescent DOM to fluorescent DOM. This appears to be true for the chromophoric fraction of DOM (and hence DOC) as well. We also note that there is an apparent loss of fluorescent DOM at the mouth of the estuary in the waters 25 to 32 psu (i.e. the location of buoy F), but no loss of chromophoric matter. However, the non-conserved behaviors are very different for the two optical pools as the F_{cDOM} to a_{g412} ratio is also non-conserved (Figure 3C and D) and indicates that there is a greater enhancement of the fluorescent DOM compared to the chromophoric DOM and this appears to be more tied to salinity compared to geographic location (i.e. chemically driven).

Every survey has demonstrated that the apparent site of non-conservative behavior in DOM is co-located with enhance particle concentrations, and that the transformation processes or input sources appear to be determined geographically and not at a certain salinity. This leads us to question the role of particulate matter in the transformation of the DOM. Our discrete particulate absorption analysis indicates that the river is always a source of chromophoric particles to the estuary compared to the marine endmember. However there is significant enhancement of particle concentration at Frankfort Flats (i.e. >factor 3) regardless of season or tidal phase. Furthermore, the composition of the particles, as indicated by spectral slope, varies significantly, with freshwater particles characterized by flat spectral slopes and marine waters by steep spectral slopes (0.008 and 0.013, generally found to correspond to new labile and older refractory material, respectively). For the two surveys in 2006, a non-conservative pattern is observed, with the site of Frankfort Flats exhibiting the flattest slopes

through the estuary, indicating that there is also transformation in the particulate matter spatially and temporally coherent with that of the dissolved matter (Figure 4). We estimated particle refractive index from observations of the particle backscattering ratio and size slope (Twardowski et al., 2001) from Frankfort Flats south through the estuary (Figure 4). Based upon the refractive index, and the absorption spectral slope, the particles at the top of the estuary appear to be mineralic (high index) but coated with labile organic matter, compared to the more detrital but less labile particles in the marine endmember.

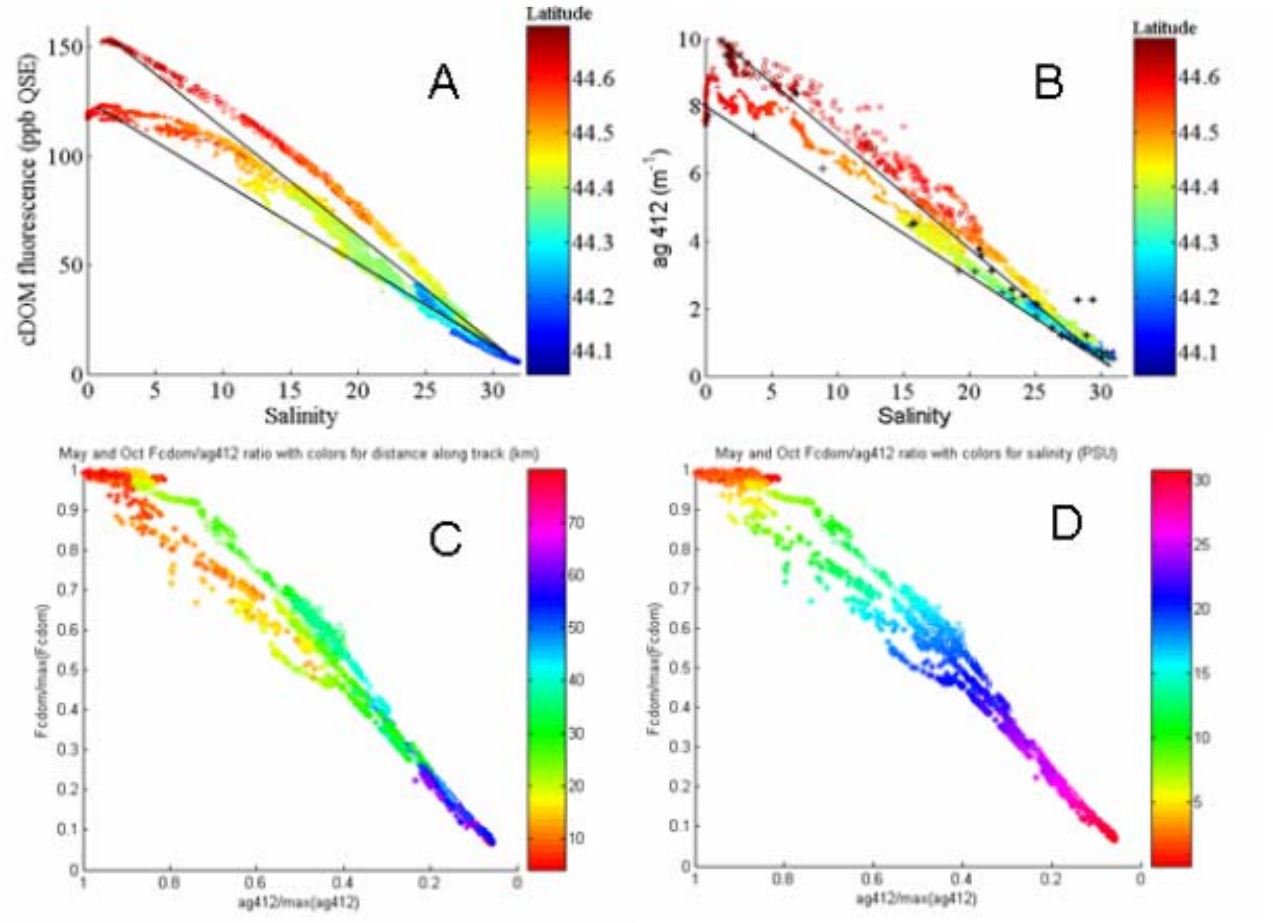

Figure 3. (A) Surface distributions of cDOM fluorescence versus salinity during the May 2006 (triangles) and October 2006 (circles) intensive field surveys. Colorbar indicates latitude. (B) Same as in E but for the dissolved absorption at 412 nm. Lines show linear mixing model, indicating enhanced fluorescence and absorption at the head of the estuary and loss of fluorescence at the mouth. (C) Surface cDOM fluorescence (normalized to maximum freshwater value) versus the dissolved absorption at 412 nm (normalized to the maximum freshwater value) for the May (circles) and October (triangles) field seasons. Colors indicate distance (km) from the river (freshwater endmember) to GoMOOS mooring F (oceanic endmember). (D) Same as in C but colors indicate surface salinity along the track.

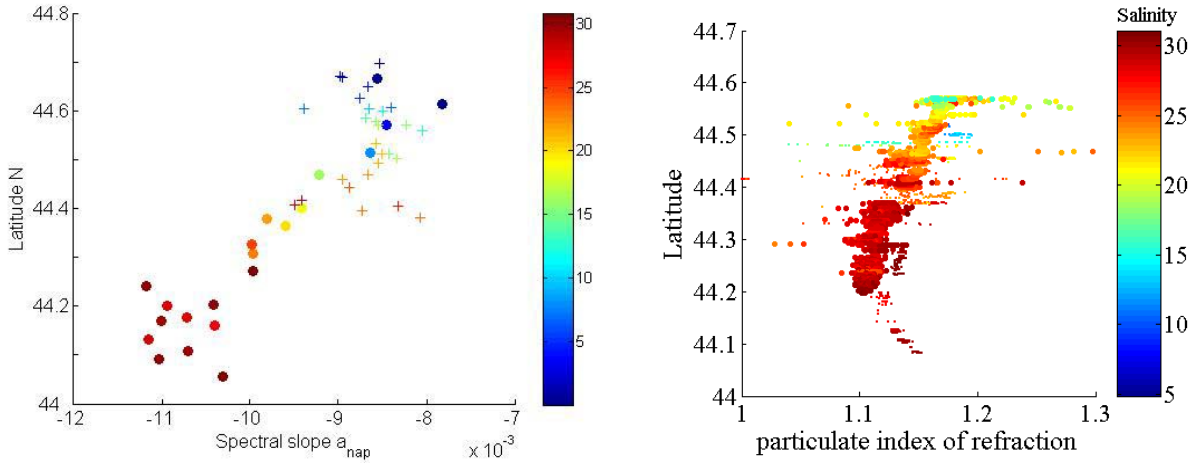

Figure 4. Left panel: The non-conserved dependence of particle composition as described by spectral slope of the non-algal particulate absorption, as a function of latitude and salinity (colorbar, psu) for May 2006 (filled circles) and October 2006 (crosses). Right panel: Surface distributions of the estimated particulate index of refraction as a function of latitude during the May 2006 (triangles) and October 2006 (circles) field seasons (colorbar, psu).

IMPACT/APPLICATIONS

The results of this study will contribute to identification of optical and biogeochemical signatures associated with specific land use activities, and quantification of the tracer potential of those signatures through the river and estuarine system to the coastal environment. The application of this approach is the capability for determining changes in terrestrial land use from autonomous observations in the river and coastal waters. Identifying the conservative and nonconservative optical and chemical variability in the dissolved and particulate fractions of river inputs will also contribute to the development of coastal and watershed models of carbon flux. The high temporal resolution data obtained in this study will allow for quantification of this variability on time scales of hours to months, covering a range of scales from daily to seasonal to interannual and including and episodic events. While the focus of this study does not address the specific transformations operating within a riverine impacted regions, these results will be useful in aiding our understanding of the relevant biogeochemical processes operating in the coastal margins influenced by riverine inputs by determining the appropriate temporal and spatial scales of optical and chemical variability that are conserved though the system.

TRANSITIONS

The USGS Augusta, ME office has shown a strong interest in transitioning the ECO triplet river observation systems we will be deploying in the Penobscot River. We will be testing these systems on a long term basis in the spring of next year and will provide results and reports on the operational performance of these systems to the USGS for their review.

RELATED PROJECTS

1. Both C. Roesler and A. Barnard are Co-PIs on a NASA sponsored multi-investigator research project examining the variability in fluxes of dissolved and particulate organic carbon from terrestrial sources to the Gulf of Maine via major rivers, and their subsequent fate within the Gulf of Maine. This work is specifically focusing on the impacts of riverine dissolved and particulate loading to the carbon cycle of coastal and offshore systems. Our ONR project is highly complementary to this project, as it is providing a better understanding of the variability in the concentration and composition of the Penobscot River dissolved and particulate materials and its subsequent delivery to the coastal and offshore regions.

2. The Gulf of Maine Ocean Observing System (GoMOOS), which Dr. Roesler is funded by to maintain optical instrumentation and data streams from the mooring observation program, is providing valuable hourly time series of coastal optical and physical surface properties upstream and downstream of the Penobscot River. Beginning in the fall of 2004, optical sensors (backscattering, chlorophyll and cDOM fluorometers) were installed on a GoMOOS mooring in the center of the mouth of the western branch of Penobscot Bay. Data from these systems are providing a wealth of information as to the hourly to seasonal variability in the dissolved and particulate materials within the river to coastal transition zone of the Penobscot Bay.

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